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Note

Comparative studies on the thermal analysis of alkali tris(carboxylato)ferrates(III)

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Because of their complexing ability and sensitivity towards oxidation, iron carboxylates are being extensively used as inorganic precursors for the production of ferrites which have useful magnetic and catalytic properties [1]. The formation of ferrites from the thermolysis of ferricarboxylate precursors (prepared by the liquid-mix technique) occurs at much lower temperatures than the conventional ceramic method. Another attractive feature of the method used is that it does not involve milling of the compound (which is necessary in the ceramic method). This milling introduces lattice defects and strains in the ferrite obtained and strongly affects its permanent magnetic properties [2].

Previously, we have successfully obtained ferrites from the thermolysis of alkaline earth ferrimalonate precursors [3,4], and in continuation of the work, the thermolysis of alkali tris(oxalato/malonato)ferrates(III) was undertaken with a view to studying the mode of decomposition of the respective precursor and obtaining a ferrite at a lower temperature. Methods of preparation and characterisation of these precursors have been reported elsewhere [5,6]. The thermal decomposition of these compounds was studied up to 1073 K in a static air atmosphere employing Mössbauer, infrared spectroscopy and non-isothermal techniques (TG, DTG and DTA), the experimental details for which are reported elsewhere [3,7].

The mode of decomposition in both the precursors, i.e. $M_3[Fe(C_2O_4)_3] \cdot xH_2O$ and $M_3[Fe(CH_2C_2O_4)_3] \cdot xH_2O$ (where M is Li, Na, K), is similar and occurs in four major consecutive steps.

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(i) Dehydration of the original complex.

(ii) Reduction of the anhydrous complex into an iron(II) species.

(iii) Reoxidation of the iron(II) intermediate to α-Fe_2O_3 of various particle sizes.

(iv) Solid state reaction between α-Fe_2O_3 and alkali metal carbonate/oxide at higher temperatures to form alkali metal ferrites.

The five-membered chelates, i.e. oxalate precursors, decompose at higher temperatures (Li, 473 K; Na, 533 K; K, 543 K) than the respective six-membered chelates, i.e. malonate precursors (Li, 463 K; Na, 503 K; K, 473 K). Irving et al. [8] studied the influence of ring size on the stability of several metal chelates and generalised that the stability decreases with increasing ring size. Erdey et al. [9], on the basis of high-temperature acid–base theory, reported that the weaker the anion base the higher the temperature of decomposition, and that the oxalate ion is a weaker anion base than the malonate ion.

The alkali metal oxalate/malonate, when present in the complex, decomposes at a lower temperature than the respective pure salt owing to (i) the catalytic action of α-Fe_2O_3 present, and (ii) the metastable structure of the oxalate/malonate formed in the former case.

Ferrites have been obtained from the thermolysis of the malonate precursor at a lower temperature (763–1013 K) than that of the oxalate precursor (1073 K). The anhydrous malonates are reported to be composed of a network of more loosely linked polymers with higher potential energy than the anhydrous oxalates [10]. These temperatures of ferrite formation are much lower than for the ceramic method [11,12].

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